Comment on "Liquids on Topologically Nanopatterned Surfaces"

In a recent letter, Gang *et al.* report measurements of liquid adsorption on substrates with geometrical structure on the nanometric scale [1]. This study is particularly interesting for a number of reasons: the chosen geometry (paraboloidal cavities), the size of the structure (in the nanometric range) and the use of two concording experimental methods (x-ray reflectivity and grazing incident diffraction). In the paper, comparison is made with the predictions of a very simple "geometrical" model for adsorption on sculpted substrates [2]. The authors compare their results with an estimation of the (asymptotic) power-law prediction of the geometrical model and conclude that they are significantly different. Here we point out that full application of the geometrical model for a finite-size (FS) paraboloid yields results which compare favourably with their experimental findings. This is to a certain extent surprising, due to the small scale of the structures, and supports previous evidence of the strong influence of surface geometry on fluid adsorption [3].
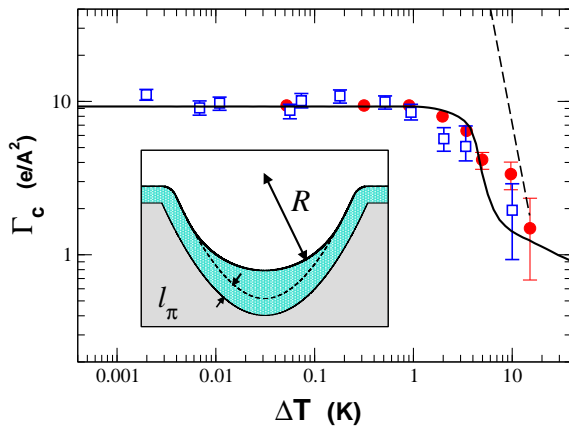

FIG. 1: Liquid adsorption Γ_c in a finite paraboloid: experimental points (symbols), prediction of the geometrical model (continuous line) and power-law estimate as published by Gang *et al.* [1] (dashed line). This line only represents the slope of the power-law, not its absolute value [5]

The inset in Fig. 1 schematically illustrates the geometrical construction as applied to a FS paraboloid. The liquid gas-interface is obtained by first coating the substrate with a layer of thickness ℓ_π followed by fitting a meniscus of radius R at the point of maximum curvature [2]. This construction requires only two length scales, the thickness of the liquid layer adsorbed on a *flat* substrate ℓ_π and the radius of curvature given by the Laplace equation R [2]. Both these quantities depend on the chemical

potential $\Delta\mu$, relative to liquid-gas coexistence. Indeed, for our particular case, we have

$$\ell_\pi(\Delta\mu) = \left(\frac{2A}{\Delta\mu\,\Delta\rho}\right)^{1/3} \qquad R(\Delta\mu) = \frac{2\sigma}{\Delta\mu\,\Delta\rho} \quad (1)$$

where $A = 1.34 \times 10^{-21}$ J is the Hamaker constant, $\sigma = 23.42$ mN/m the liquid-gas surface tension and $\Delta\rho = 4.6956$ nm^{-3} the density difference between the coexisting phases [1, 4].

This procedure allows one to predict a number of geometrical quantities as a function of $\Delta\mu$, including the adsorption in the paraboloidal cavity, Γ_c. This quantity is plotted in Fig. 1 together with the experimental results of Gang *et al.* as a function of the temperature difference between the substrate and the gas ΔT (instead of $\Delta\mu$) in line with the authors [1]. Despite the simplicity of the model, there is an overall agreement between theory and experimental data. We want to emphasise here that the theory has *no adjustable parameters*.

There are three regimes: I) For $\Delta T \gtrsim 8K$, no meniscus is present and the adsorption is essentially $\ell_\pi A_r$, where A_r is the *real* area of the substrate (as opposed to the projected area), II) For $5 \lesssim \Delta T \lesssim 8K$, the adsorption is strongly sensitive to saturation conditions due to the sudden rise of the liquid meniscus, and III) For $\Delta T \lesssim 5K$, the meniscus is essentially "pinned" to the rim of the paraboloid and the increase in adsorption is only due to its changing radius R. As predicted [2], the rise of the meniscus is so abrupt in regime II that the finite paraboloid fills almost completely for a small change in ΔT. Thus, the asymptotic regime is essentially undetectable (bound closely by regimes I and III) and a comparison of the experimental adsorption with a mere power-law (see Fig. 1) indicates unwarrantedly that the predictions of the geometrical model are inadequate for the finite paraboloid.

Note as well that the abrupt filling takes place at a value of $\Delta\mu$ strongly dependent on the geometry of the cavities and, therefore, any dispersity in the shape or size of the experimental cavities (apparent in Fig. 1(a) of [1]) will smooth the adsorption curve yielding a smaller (effective) value of the exponent β_c and, perhaps, be responsible for the small discrepancies at high ΔT.

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